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(54) **Disperse-reactive dyes suitable for dyeing and printing polyester-cellulose blended fibres.**

(57) Disperse–reactive dyes suitable for dyeing and printing, in one step only, polyester-cellulose blended fibres are described, which are comprised in the general formula

$$D - (SO_2 - C_2H_4OCOR)_n$$

wherein :

D is the residue of the molecule of a dye of the azo, anthraquinone methinic or quinophthalonic series, free from solubilizing groups such as the sulphonic and the carboxylic groups;

n is a number equal to 1 or 2;

R is an alkyl C_1-C_8, optionally substituted by halogen or CN; an alkenyl C_2-C_8, optionally substituted by halogen or CN; an alkoxyl C_1-C_8; a cycloalkoxyl; HN-alkyl C_1-C_4; HN-halogen alkyl C_1-C_4; N(alkyl C_1-C_4)$_2$.

Methods of preparing the dyes and of applicating same on said blends are described as well.

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This invention relates to a new series of dyes which are employed for dyeing and printing polyester-cellulose blended material.

Processes are known for dyeing polyester-cellulose blended fibres which comprise more than one step, according to which the blend components are dyed in separate steps with different dyes (disperse dyes plus reactive dyes; disperse dyes plus vat dyes).

These processes exhibit serious drawbacks such as complexity of execution, possibility of reciprocal staining, necessity of using considerable amounts of dyes.

One of these dyeing processes is described, for example, in U.S. patent 3,313,590.

Processes for dyeing polyester-cellulose blended fibres employing only one dye in one step only are known too, the best known of them being the one utilizing the swelling action exerted by water on cellulose.

This process exhibits the drawback of requiring the use of an organic solvent subject to evaporate or decompose at the

high temperatures at which it is operated, usually around 200°C, so causing problems of environmental pollution. Furthermore the solvent, being water-soluble, pollutes the waste waters.

Moreover, the materials dyed according to such process exhibit low values of stability to moisture and sublimation due to the fact that the dyes employed do not bind to the cellulose component of the blend.

This process is described, for example, in U.S. patent 3,706,525.

Another process, described in Japanese patent application 7,306,932, permits to use only one dye for dyeing the blend and offers the advantage, as compared with the preceding process, of not employing any solvent, since it is based on dyes having a reactive group of the type $CH_2=CHSO_2-$ capable, besides of binding to the cellulose component, also of fixing on the polyester component of the blend.

Such dyes, however, exhibit some limitations in the covering power and in the fixing power on the blend, with consequent shade variations on the two components of said blend and unsatisfactory yields; also fastness to light is poor.

It is an object of the present invention to provide a new series of disperse reactive dyes carrying at least a variously acylated beta-hydroxyethylsulphonyl group, which are free from solubilizing groups such as the sulphonic and the carboxylic groups, suited to dye and print, in one step, polyester-cellulose blended fibres, as well as to provide the methods of utilizing and preparing same.

More in particular the present invention relates to disperse-reactive dyes of general formula :

$$D-(SO_2C_2H_4OCOR)_n \qquad (I)$$

wherein :

D is the residue of the molecule of a dye of the azo, anthraquinone, methinic or quinophthalonic series, free from solubilizing groups such as the sulphonic and the carboxylic groups;

n is a number equal to 1 or 2;

R is an alkyl C_1-C_8, preferably C_1-C_4, optionally substituted by halogen or CN; an alkenyl C_2-C_8, optionally substituted by halogen or CN; an alkoxyl C_1-C_8; a cycloalkoxyl; HN--alkyl C_1-C_4; HN-halogen alkyl C_1-C_4; N(alkyl C_1-C_4)$_2$.

The dyes of general formula (I) are prepared, as illustrated hereinafter, by condensation of the intermediate of general formula :

$$D-(SO_2C_2H_4OH)_n \qquad (II)$$

with a proper acylating agent; among such agents the preferable ones are the following :

R_1COCl (III) $\qquad (R_2)_2NCOCl$ (IV) $\qquad (R_3CO)_2O$ (V)

$R_4OOC-Cl$ (VI) $\qquad R_5-N=C=O$ (VII)

wherein : D and n have the meanings specified hereinbefore, and :

R_1 is an alkyl C_1-C_8, optionally substituted by halogen or CN; an alkenyl C_2-C_8, optionally substituted by halogen or CN;

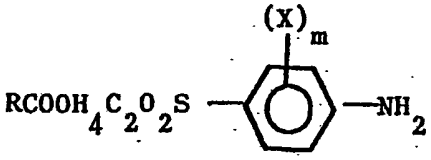
R_2 is an alkyl C_1-C_4;

R_3 is an alkyl C_1-C_8;

R_4 is an alkyl C_1-C_8, optionally substituted by halogen;

R_5 is an alkyl C_1-C_4, a halogen alkyl C_1-C_4.

An alternative method of synthetizing the azo dyes may consist in diazotizing, in an aqueous acid medium, an amine of general formula :



(VIII)

and in successively coupling, always in an aqueous medium, diazonium salt on a suitable coupling intermediate, such as, for example, the ones exemplified in the formulas from (XI) to (XIV); or in diazotizing an amine of formula :

$$Ar - NH_2 \qquad (IX)$$

and in coupling the resulting diazo on a coupling intermediate of formula :

$$Cop - SO_2C_2H_4OCOR \qquad (X)$$

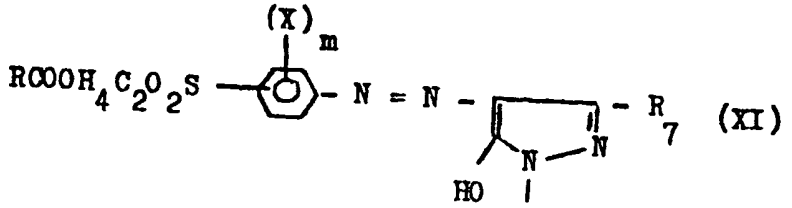
such as, for example, the one exemplified in formula (XV); wherein : R has the meaning previously defined, and : X is H, a halogen, CN, NO_2, an alkyl C_1-C_4, an alkoxyl C_1-C_4; m is a number equal to 1 or 2; Ar is the residue of a diazotizable component of the carbocyclic or heterocyclic series, and Cop is the residue of a coupling component.

The reaction between the intermediates of general formula (II) and the reagents of general formulas (III) to (VII), as well as the reactions for obtaining the intermediates having formula (VIII) and (X) respectively are generally conduct-

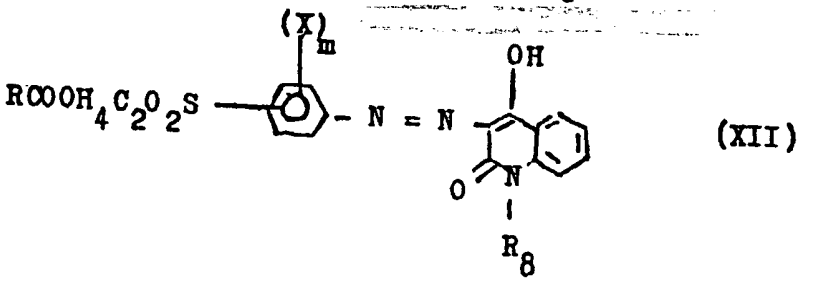
ed in the presence of aprotic solvents such as, for example, benzene, toluene, xylene, chlorobenzene, orthodichlorobenzene, pyridine, dimethylformamide, dimethylsulphoxide, at temperatures of from 0° to 140°C optionally in the presence of basic catalysts such, for instance, pyridine or acid acceptors such as e.g. triethylamine.

Generally the dyes of general formula (I) possess a high purity degree, so that no purification is required.

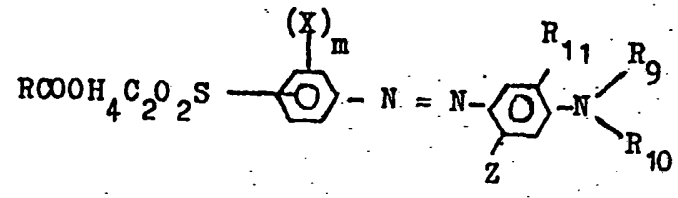
In the series of the disperse—reactive dyes forming the object of the present invention, the preferential classes of dyes result to be the ones corresponding to the following formulas:



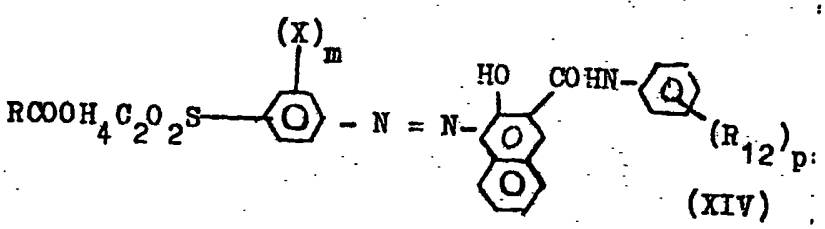
(XI)



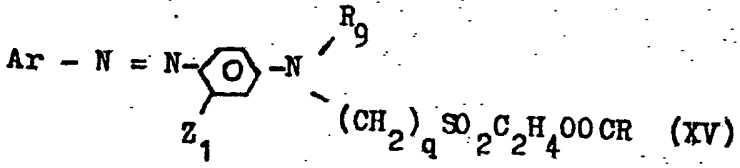
(XII)



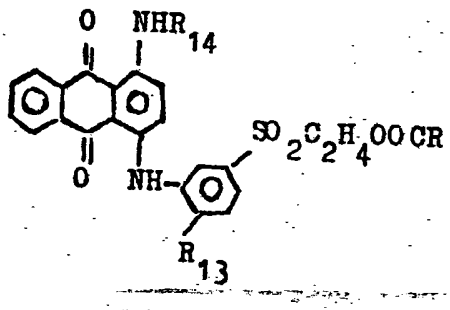
(XIII)



(XIV)



(XV)



(XVI)

wherein :

R, X, m, Ar have the meanings specified hereinbefore, and :

R_6 is H; an alkyl C_1-C_4, an aryl (e.g. phenyl) optionally substituted by 1 or 2 atoms of Cl or by a group SO_2N(alkyl C_1-C_4)$_2$;

R_7 is an alkyl C_1-C_4, COO alkyl C_1-C_4;

R_8 is H, an alkyl C_1-C_4, a hydroxyalkyl C_1-C_4;

R_9 and R_{10} like or unlike each other, are each an alkyl C_1-C_4;

a cyanoalkyl C_1-C_4, a hydroxyalkyl C_1-C_4, an alkoxy--alkyl C_1-C_4, a halogen alkyl C_1-C_4, an alcyloxy-alkyl C_1-C_4, an aralkyl;

R_{11} is H, a halogen, an alkyl C_1-C_4, an alkoxyl C_1-C_4;

R_{12} is H, a halogen, an alkyl C_1-C_4, an alkoxyl C_1-C_4;

R_{13} is H, an alkyl C_1-C_4, an alkoxyl C_1-C_4, a halogen;

R_{14} is H, CO alkyl C_1-C_8, optionally substituted, CO alkenyl C_2-C_8, optionally substituted, CO alkoxyl C_1-C_8, CO cycloalkoxyl, COHN alkyl C_1-C_4, COHN halogen alkyl C_1-C_4, CON(alkyl C_1-C_4)$_2$;

p is a number from 1 to 3;

q is a number equal to 2 or 3;

Z is H, an alkyl C_1-C_4, a halogen, a group NHCO alkyl C_1-C_4;

Z_1 is H, an alkyl C_1-C_4, a halogen.

The dyes of --------- the present invention are particularly suitable for continuously dyeing according to the pad--steam method or to the pad-thermosol method, and for printing "shade on shade" the polyester-cellulose blended fibres imparting to them shades varying from greenish yellow to greenish blue, characterized by a high fixing and by good stabilities to light, sublimation, washings as well as to friction in dry and wet conditions.

As compared with the dyes of the prior art, the dyes of general formula (I) exhibit an easy receptivity and excellent applicative properties as regards the covering of the blend (absence of any shade variations on the two fibres forming the blend), the fixability and the dye yield (capability of providing intense shades).

Also the stabilities to sublimation and to rubbing appear excellent.

That can be obtained in particular by using the dyes belonging to the preferential classes.

The dyes of general formula (I) preliminarily ground in the presence of proper dispersants (such as, for example, the one obtained by condensation between beta-naphthalene sulphonic acid and formaldehyde) up to a particle size of 0.5 - 1 μ, are applicated on the polyester-cellulose blended fibres in the form of a liquid or of an aqueous paste, additioned with an alkaline substance, preferably sodium bicarbonate or sodium phosphate, and with an auxiliary component, such as e.g. Anionico OL 495 (R), Antarox CO 430 (R) or Tanaprint ASD (R) either alone or in admixture with one another in amounts varying from 10 to 40 g/kg of printing paste.
Similar results are obtained by using substances which, though they are initially not alkaline, generate alkalis during the process; sodium trichloroacetate is particularly effective.

The printing pastes contain also other additives such as urea, in the amount of 50-100 g/kg of printing paste, and oxidants such as sodium m-nitrobenzene sulphonate.

The fixing of the dye on the blend is obtained by subjecting the dyeings and printings to heating treatments by means of dry air (Thermosol process) or superheated steam (HT process) at temperatures ranging from 170°C to 220°C for stretches of time of from 1 minute to 10 minutes.
Successively the dyed or printed blended fibres are subjected to a cleaning process in a bath containing soap or a synthetic detergent and a suitable alkaline agent such as e.g.

sodium carbonate and/or sodium hydrate, in order to remove not fixed dye, if any.

The blends suited to be dyed and printed with the dyes of general formula (I) include cellulose fibres in the natural form such as, for example, cotton and flax, or in the regenerated form such as, for example, viscose. The blends may include furthermore polyethylene terephthalate as polyester component.

Although the ratio between polyester component and cellulose component of the blend is not critical, it is preferable to employ blends having a cellulose-polyester ratio ranging from 80:20 to 20:80.

The following examples are given to illustrate the characteristics of the present invention, without being however a limitation thereof.
Unless otherwise specified, the term "parts" is to be understood as expressed in weight units.

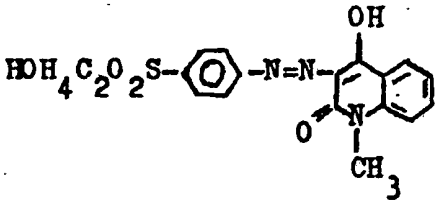
EXAMPLE 1

4.02 parts of 4-hydroxyethylsulphonyl aniline were dispersed with 8.0 parts by volume of HCl. d = 1.18 and with 40 parts by volume of water.
The mass was cooled down to 0-5°C and in 5 minutes a solution of 1.4 parts of $NaNO_2$ in 10 parts by volume of water was poured thereinto.
It was stirred at 0-5°C for 1 hour whereupon HNO_2 in excess was eliminated by sulphamic acid.

The diazo solution was clarified and poured at 5-10°C into a solution of 3.5 parts of 1-methyl-4-hydroxy-2-quinolone in 40 parts by volume of water and 1.0 part of NaOH; during coupling the pH was maintained alkaline by addition of sodium carbonate.

On conclusion of coupling it was filtered, the precipitate was washed to neutrality with water and dried.

6.9 parts of the following azoic intermediate were obtained :

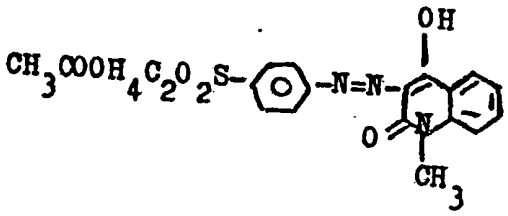


Such intermediate - 6.9 parts - was successively treated at boiling temperature for 2 hours with 8.0 parts by volume of acetic anhydride.

The mass was allowed to cool down, then it was poured into 100 parts by volume of water.

After having stirred the mass for 1 hour, it was filtered and the precipitate was washed to neutrality.

The cake was dried, so obtaining 7.2 parts of the dye :



40 parts of such dye were microfined with 40 parts of Saltetra F (a condensate between beta-naphthalene sulphonic acid and formaldehyde), 25 parts of ethylene glycol, 1 part of Parmetol DF12(R) and 94 parts of water.

Using 150 parts of such mixture, 1,000 parts of printing paste were prepared by addition of 60 parts of urea, 10 parts of sodium m-nitro-benzene sulphonate, 500 parts of a solution of sodium alginate at 10%, 10 parts of sodium bicarbonate, 20 parts of Tanaprint ASD (R) (a mixture of alkylphenol oxyethylenate and oleic acid oxyethylenate) and 250 parts of water. Such paste was applicated on a fabric of polyester-cotton (65:35) blended fibres, ready for printing, whereupon said paste was allowed to dry at a temperature below 100°C.

The fixing of the dye on the two fibres constituting the blend was effected: a) in a thermosol apparatus operating at 210°C for 60 seconds, b) in a steaming apparatus operating at 180°C for 8 seconds.

The printing, either heat set or steamed, was subjected to a cleaning process in three steps :

1) cold and hot washing,
2) soaping at 90°C for 10 minutes with 3 g/l of sodium hydrate, 3 g/l of sodium carbonate, 2 g/l of detergent Diapon T (R) and 2 g/l of ethylene diamine tetra-acetate,
3) rinsing.

A greenish yellow printing, perfectly hidden and exhibiting a uniform shade was obtained.

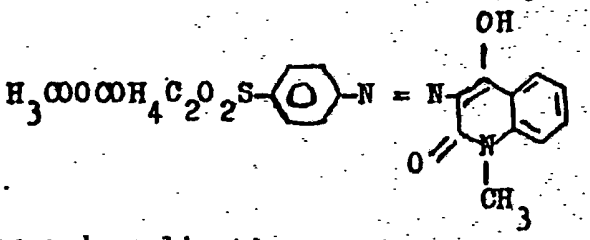
The strength obtained was 1/1 (E.C.E.). Good stabilities to light, to moist washings and trichloroethylene cleaning, and to friction corresponded to such strength.

EXAMPLE 2

10 parts of the azoic intermediate of example 1 were dissolved with 60 parts by volume of pyridine; the solution was cooled to 0-10°C and 14 parts by volume of methyl chloroformate were then gradually added.

The reaction continued for 2 hours at 0-10°C, whereupon the solution was poured into 300 parts of water. It was stirred for about 30 minutes, then it was filtered and the cake was repeatedly washed with water.

By drying it was possible to obtain 9.4 parts of the dye :

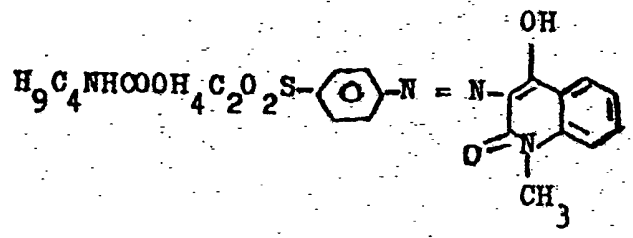


Microfining and application were carried out by operating under the same conditions as in the preceding example, so obtaining a greenish yellow printing with characteristics similar to the ones of example 1.

EXAMPLE 3

10 parts of the azoic intermediate of example 1 were reacted at 130-140°C for 10 hours with 2.8 parts of butyl isocyanate and 35 parts by volume of ortho-dichlorobenzene.

At the end of the reaction the mass was allowed to cool, then it was filtered, washed with a few petroleum ether and dried. 10.7 parts of the following dye were obtained :



Microfining and application were effected under the same conditions of example 1, so obtaining a greenish yellow printing having characteristics similar to the ones of said example.

EXAMPLE 4

4.62 parts of 2-methoxy-5-hydroxyethylsulphonyl-aniline were dispersed with 8.0 parts by volume of HCl d = 1.18 and with 40 parts by volume of water.

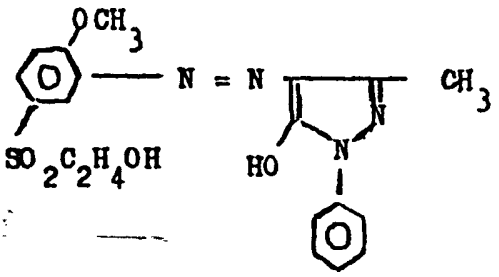
The mass was cooled down to 0-5°C and a solution of 1.4 parts of $NaOH_2$ in 10 parts by volume of water was poured thereinto in about 5 minutes.

It was stirred at 0-5°C for 1 hour, then the HNO_2 in excess was eliminated with sulphamic acid.

The diazo solution was clarified and poured at 0-5°C into a solution of 3.5 parts of 1-phenyl-3-methyl-2-pyrazol-5-one in 40 parts of water and 1.0 parts of NaOH.

At the end of coupling it was filtered, the precipitate was washed to neutrality with water and dried.

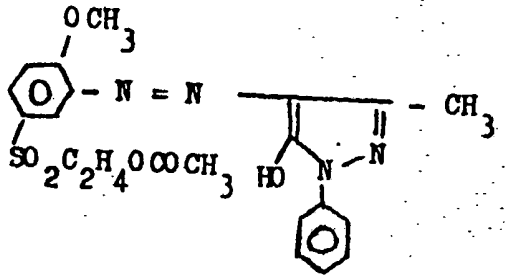
6.7 parts of the following azoic intermediate were obtained :



3.4 parts of the above intermediate were treated at boiling temperature for 30 minutes with 10 parts by volume of acetic anhydride.

The mass was allowed to cool, whereupon it was poured into 100 parts by volume of water. After stirring for further 30 minutes it was filtered and the precipitate was washed to neutrality with water.

The cake was dried, so obtaining 3.5 parts of the dye :

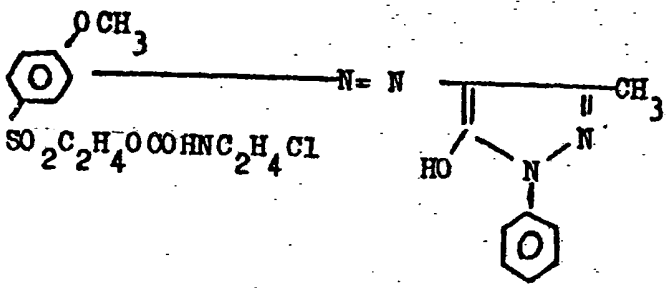


By effecting both micrifining and application under the conditions of example 1 it was possible to obtain a perfectly hidden and uniform yellow printing endowed with good stabilities to light, moist washings and trichloroethylene cleanings, as well as to friction.

EXAMPLE 5

4.1 parts of the azoic intermediate of example 4 were reacted with 1.1 parts of chloroethyl-isocyanate in the presence of 15 parts by volume of chlorobenzene at 120°C for 10 hours. At the conclusion the mass was cooled to room temperature, was filtered, washed with a few petroleum ether and dried.

4.9 parts of the following dye were obtained :



which, after having been microfined and applicated under the conditions of example 1, provided a yellow shade printing having characteristics similar to the ones of example 4.

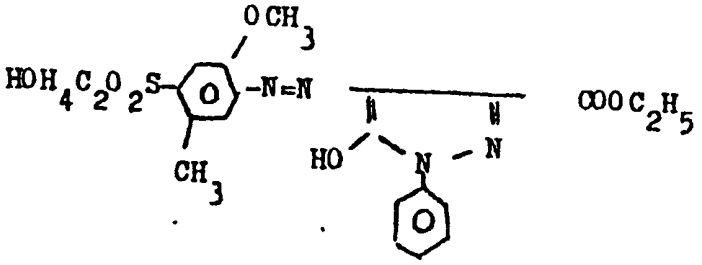
EXAMPLE 6

4.9 parts of 2-methoxy-4-hydroxyethylsulphonyl-5-methyl-aniline were diazotized according to the modalities described in

example 4 and coupled on 4.64 parts of the ethyl ester of 1-phenyl-2-pyrazol-5-one-3-carboxylic acid in solution with 40 parts by volume of acetic acid and 20 parts by volume of water.

During coupling the pH of the mass was maintained at 4-5 by addition of sodium acetate in crystals.

It was then operated as described in example 4, so obtaining 9.2 parts of the intermediate dye :

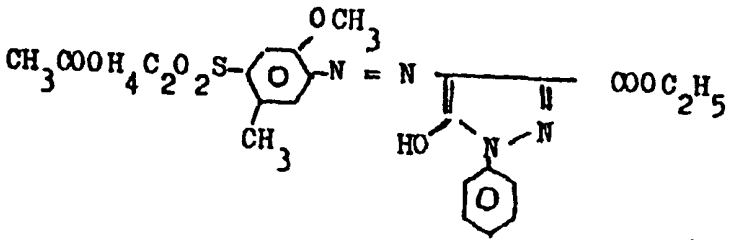


4.9 parts of such intermediate were successively reacted at boiling temperature for 1 hour with 10 parts of acetic anhydride.

The whole was allowed to cool down to room temperature, whereupon it was poured into 80 parts by volume of water.

After having stirred the mass for 1 hour, it was filtered and the precipitate was washed to neutrality with water.

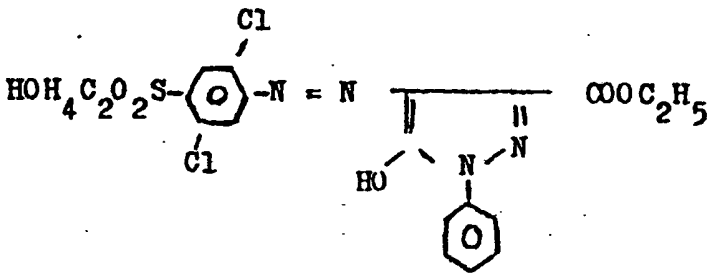
The cake was dried, so obtaining 5.0 parts of the dye :



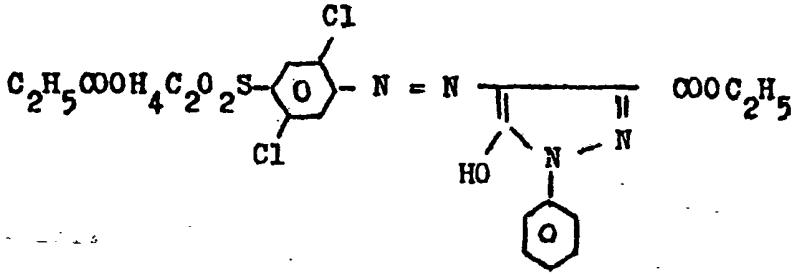
which, after having been microfined and applicated under the conditions of example 1, provided a perfectly hidden and uniform reddish yellow printing having good general stabilities.

EXAMPLE 7

5.4 parts of 2.5-dichloro-4-hydroxyethylsulphonyl-aniline were diazotized and coupled on 4.65 parts of the ethyl ether of 1-phenyl-2-pyrazol-5-one-3-carboxylic acid according to the modalities described in example 6.
10.85 g of the azoic intermediate :



were obtained, which were reacted with 15 parts by volume of propionic anhydride for 2 hours at boiling temperature. It was then operated as described in example 6, so obtaining 11.0 parts of the dye :



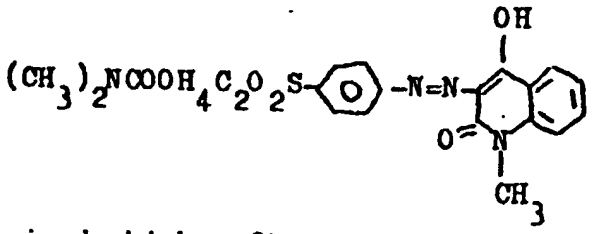
which, after having been microfined and applicated under the conditions described in example 1, provided a reddish yeallo printing having characteristics similar to the ones of example 6.

EXAMPLE 8

3.9 parts of the azoic intermediate of example 1 were reacted at 100°C for 8 hours with 1.1 parts of dimethyl carbamyl chloride in the presence of 30 parts by volume of xylene.

On completion of the reaction the mass was cooled to room temperature and the separated precipitate was recovered by filtration,was washed with a few petroleum ether and dried.

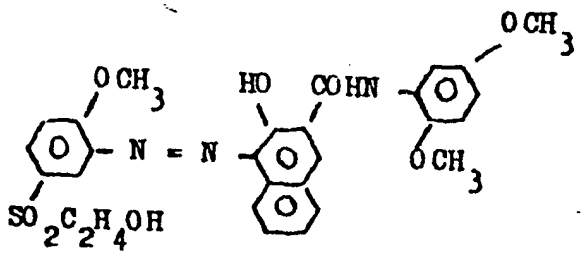
4.8 parts of the dye :



were obtained which, after micrifining and application under teh conditions described in example 1, provided a yellow shade printing having characteristics similar to the ones described in such example.

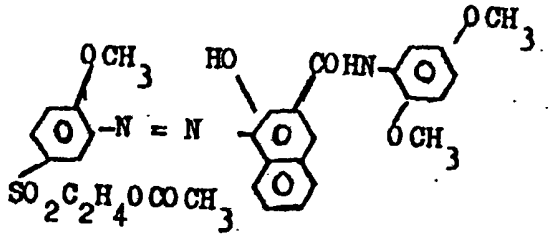
EXAMPLE 9

4.62 parts of 2-methoxy-5-hydroxy-ethyl-sulphonyl-aniline were diazotized according to the modalities illustrated in example 4 and were coupled on 6.46 parts of 2,5-dimethoxy-anilide of 2-hydroxy-3-naphthoic acid in 50 parts of water and 5.0 parts of NaOH; during coupling the pH of the mass was maintained alkaline by addition of Na_2CO_3.
By operating according to example 4 it was possible to obtain 10.8 parts of the following azoic intermediate :



5.65 parts of which were reacted at boiling temperature

for 30 minutes with 10 parts by volume of acetic anhydride. By proceeding then as described in example 4, 5.7 parts of the following dye were obtained :

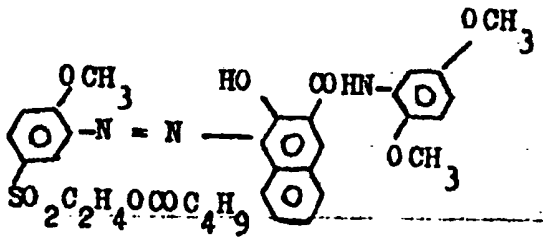


The dye was microfined under the conditions of example 1. From 100 parts of such mixture 1000 parts of printing paste were prepared by addition of 80 parts of urea, 10 parts of sodium m-nitro-benzene sulphonate, 500 parts of a solution of sodium alginate at 10%, 10 parts of sodium bicarbonate, 40 parts of Tanaprint ASD(R) and 260 parts of water. By operating according to example 1 a perfectly hidden and uniform red shade printing, having a strength of 1/1 (E.C.E.) and good general stabilities was obtained.

EXAMPLE 10

5.05 parts of the intermediate azo-dye of example 9 were reacted at 100°C for about 8 hours with 1.3 parts of the chloride of n-pentanoic acid in 20 parts by volume of chlorobenzene and 0.8 parts by volume of pyridine.

At the conclusion of the reaction the mass was cooled to room temperature, then it was filtered and washed with a few petroleum ether. By drying it was possible to obtain 6.2 parts of the dye :



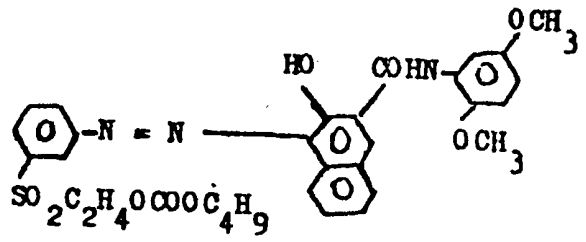
which, after having been microfined and applicated under the conditions described in example 9, provided a red shade printing having characteristics similar to those illustrated in example 9.

EXAMPLE 11

2.01 parts of 3-hydroxy-ethyl-sulphonyl-aniline were diazotized and coupled, according to the modalities of example 1, on 3.23 parts of the 2.5-dimethoxy-anilide of 2-hydroxy-3-naphthoic acid.

The intermediate azo-dyes obtained - 5.1 parts - was reacted, under the conditions described in example 2, with 8.0 parts by volume of butyl chloroformate.

It was operated analogously with such example, so obtaining 5.2 parts of the dye :



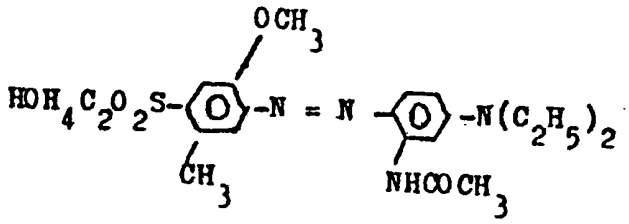
which, after having been microfined and applicated under the conditions of example 9, provided a perfectly hidden and uniform yellowish red printing having good general stabilities.

EXAMPLE 12

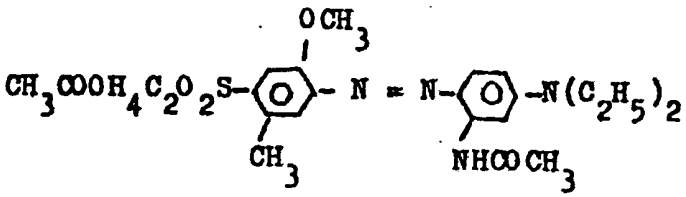
4.9 parts of 2-methoxy-4-hydroxy-ethyl-sulphonyl-5-methyl-aniline were diazotized and coupled, according to the method described in example 6, on 4.12 parts of N.N-diethyl-m-aminoacetanilide in 40 parts of water and 5 parts by volume of HCl

d = 1.18. During coupling the pH of the mass was maintained at 4-5 by addition of sodium acetate in crystals.

By operating then according to example 6, it was possible to obtain 8.9 parts of the intermediate azo-dye :



4.62 parts of such intermediate were reacted at boiling temperature for about 30 minutes with 6 parts of acetic anhydride. It was successively operated as described in example 1, so obtaining 4.5 parts of the dye :



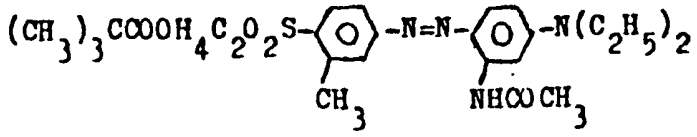
which, after having been microfined and applicated under the conditions of example 9, provided a perfectly hidden and uniform scarlet shade printing having good general stabilities.

EXAMPLE 13

4.62 parts of the azoic intermediate of example 12 were reacted with 1.9 parts of pivalic anhydride in the presence of 1.1 parts of triethylamine and 25 parts by volume of dimethylformamide at a temperature of about 40°C for about 2 hours.

At the end of the reaction the solution was poured into 200 parts of water, it was stirred for 30 minutes, whereupon the resulting precipitate was filtered and washed with water.

By drying 4.8 parts of the following dye were obtained :

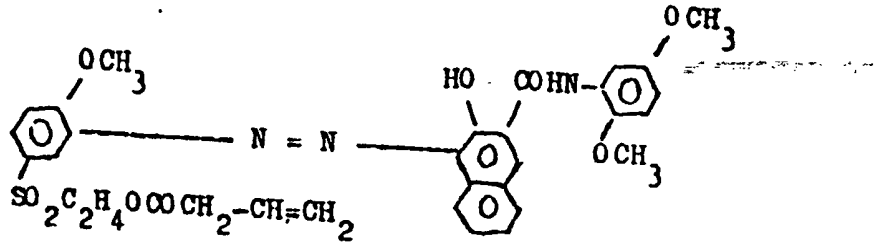


which, after having been microfined and applicated under the conditions already described hereinbefore, provided a scarlet shade printing having characteristics similar to the ones illustrated in example 12.

EXAMPLE 14

5.65 parts of the azoic intermediate of example 9 were reacted at 80°C for 12 hours with 1.2 parts of the chloride of vinyl acetic acid in 25 parts by volume of xylene and 0.8 parts by volume of pyridine.

At the conclusion of the reaction the mass was cooled to room temperature, then it was filtered and washed with a few petroleum ether. By drying it was possible to obtain 5.7 parts of the dye :



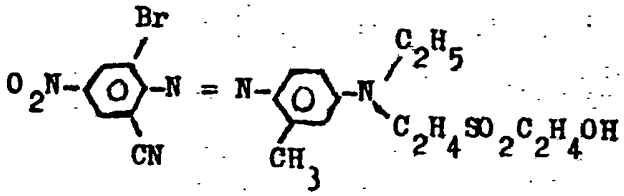
which, after having been microfined and applicated under the described conditions, provided a red shade printing exhibiting characteristics analogous with the ones of example 9.

EXAMPLE 15

4.84 parts of 2-bromo-4-nitro-6-cyanoaniline were added, at 0-5°C and in 1 hour, to a solution consisting of 1.38 parts of sodium nitrite in 40 parts by volume of H_2SO_4 d = 1.84. It was then stirred for 30 minutes whereupon the diazo solution was poured, at 5-10°C, into a solution of 5.46 parts of N-ethyl-N-(hydroxy-ethyl-sulphonyl)-ethyl-m-amino-toluidine in 40 parts of water and 2.0 parts by volume of HCl d = 1.18. During coupling the pH of the mass was maintained at 4-5 by addition of sodium acetate in crystals.

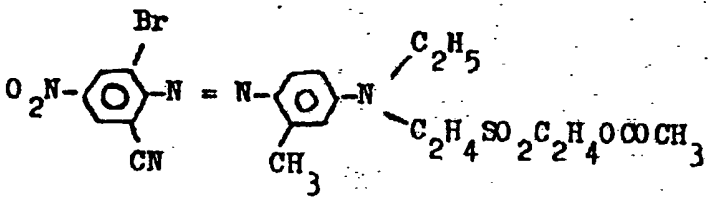
After stirring for 1 hour it was filtered and the precipitate was washed with water.

The cake was dried, so obtaining 10.3 parts of the following intermediate dye :



5.26 parts of such intermediate azo-dye were reacted with 10 parts by volume of acetic anhydride for 40 minutes at boiling temperature.

It was then operated according to example 1, so obtaining 5.3 parts of the dye :



which, after having been microfined and applicated under the

conditions of example 1, provided a perfectly hidden bluish violet printing having a uniform shade and good general stabilities.

EXAMPLE 16

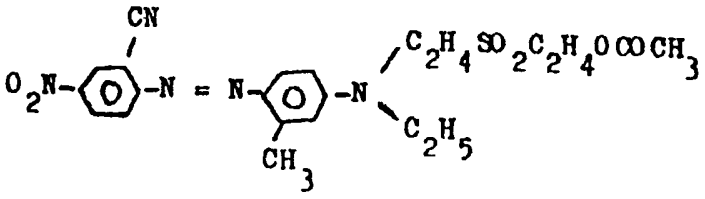
A solution of 3.26 parts of 2-cyano-4-nitro-aniline in 30 parts of acetic acid, 8 parts of propionic acid and 4 parts of water was cooled to 5-10°C and then additioned, in about 1 hour, with 20 parts by volume of nitrosyl sulphuric acid 1N.

After stirring for about 1 hour at 5-10°C, the diazo solution was gradually poured nto the mass obtained by reacting 5.46 parts of N-ethyl-N-(hydroxyethylsulphonyl)-ethyl-m-amino-toluidine with 10 parts by volume of acetic anhydride, then it was boiled for 20 minutes and successively cooled to 5-10°C.

During coupling the pH was maintained at 4-5 by addition of sodium acetate in crystals.

It was filtered after 1 hour, then the precipitate was washed with water and dried.

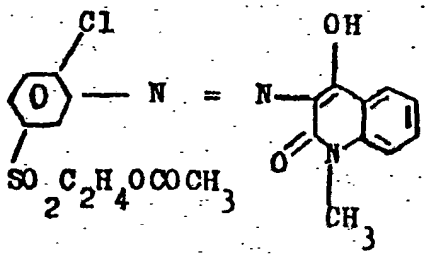
8.3 parts of the dye :



were obtained, which, after having been microfined and applicated under the conditions of example 1, provided a perfectly hidden ruby printing having a uniform shade and good general stabilities.

EXAMPLE 17

5.55 parts of 2-chloro-5-acetoxyethyl-sulphonyl aniline were diazotized and coupled, according to the modalities described in example 1, on 3.5 parts of 1-methyl-4-hydroxy-2-quinolone. 8.8 parts of the dye :

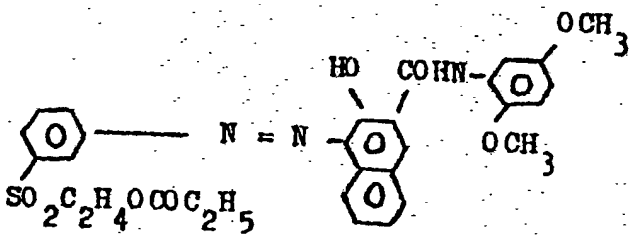


were obtained which, after having been microfined and applicated under the conditions already described, provided a perfectly hidden yellow printing having a uniform shade and good general stabilities.

EXAMPLE 18

5.14 parts of 3-propioxyethylsulphonyl-aniline were diazotized and coupled on 6.46 parts of 2.5-dimethoxy anilide of 2-hydroxy-3-naphthoic acid according to the modalities described in example 9.

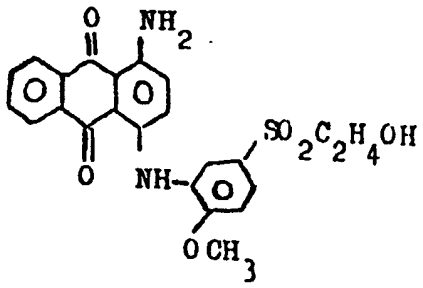
11.2 parts of the dye :



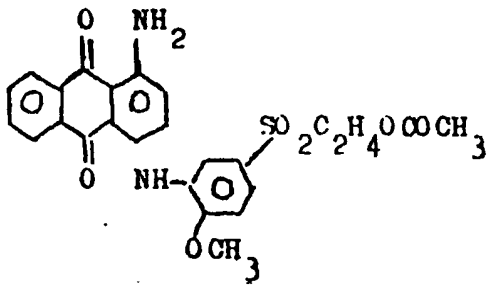
were obtained, which provided a perfectly hidden yellowish red printing having a uniform shade and good general stabilities.

EXAMPLE 19

6.2 parts of 2-methoxy-5-hydroxy-ethylsulphonyl aniline were reacted at 95°C for 2 hours with 5.31 parts of 1-amino-4-bromo-2-anthraquinone-sulphonic acid in the presence of 8.8 parts of $NaHCO_3$ and 1.0 part of cuprous chloride.
At the conclusion of the reaction the mass was cooled to 50°C, acidified with HCl d = 1.18 to a pH value = 1-2 and filtered.
The precipitate was washed with a slightly acid solution containing sodium chloride and was successively treated with 8.0 parts of 30% sodium hydrate and 3.0 parts of glucose for 1 hour at 90°C.
After filtering, washing with water and drying, 4.25 parts of the anthraquinone intermediate :



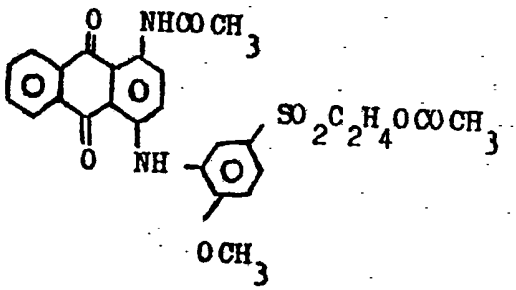
were obtained.
4.0 parts of such intermediate were dissolved in 9.0 parts of H_2SO_4 d = 1.5 and additioned, at room temperature and in 6 hours, with 6.0 parts of acetic anhydride. The solution was stirred for about 24 hours, whereupon it was diluted with water, filtered and washed to neutrality with water.
After drying, 3.4 parts of the dye :



were obtained, which, after having been microfined and applicated under the conditions illustrated in example 9, provided a perfectly hidden neutral blue printing, having a uniform shade and good general stabilities.

EXAMPLE 20

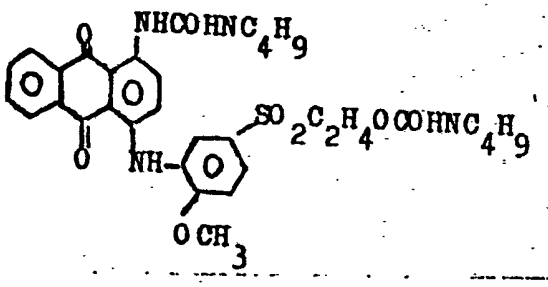
4.52 parts of the anthraquinone intermediate of example 19 were reacted, at boiling temperature for 60 minutes, with 12 parts by volume of acetic anhydride.
By operating then as described in example 1 it was possible to obtain 4.8 parts of the dye :



which provided a perfectly hidden violet printing having a uniform shade and good general stabilities.

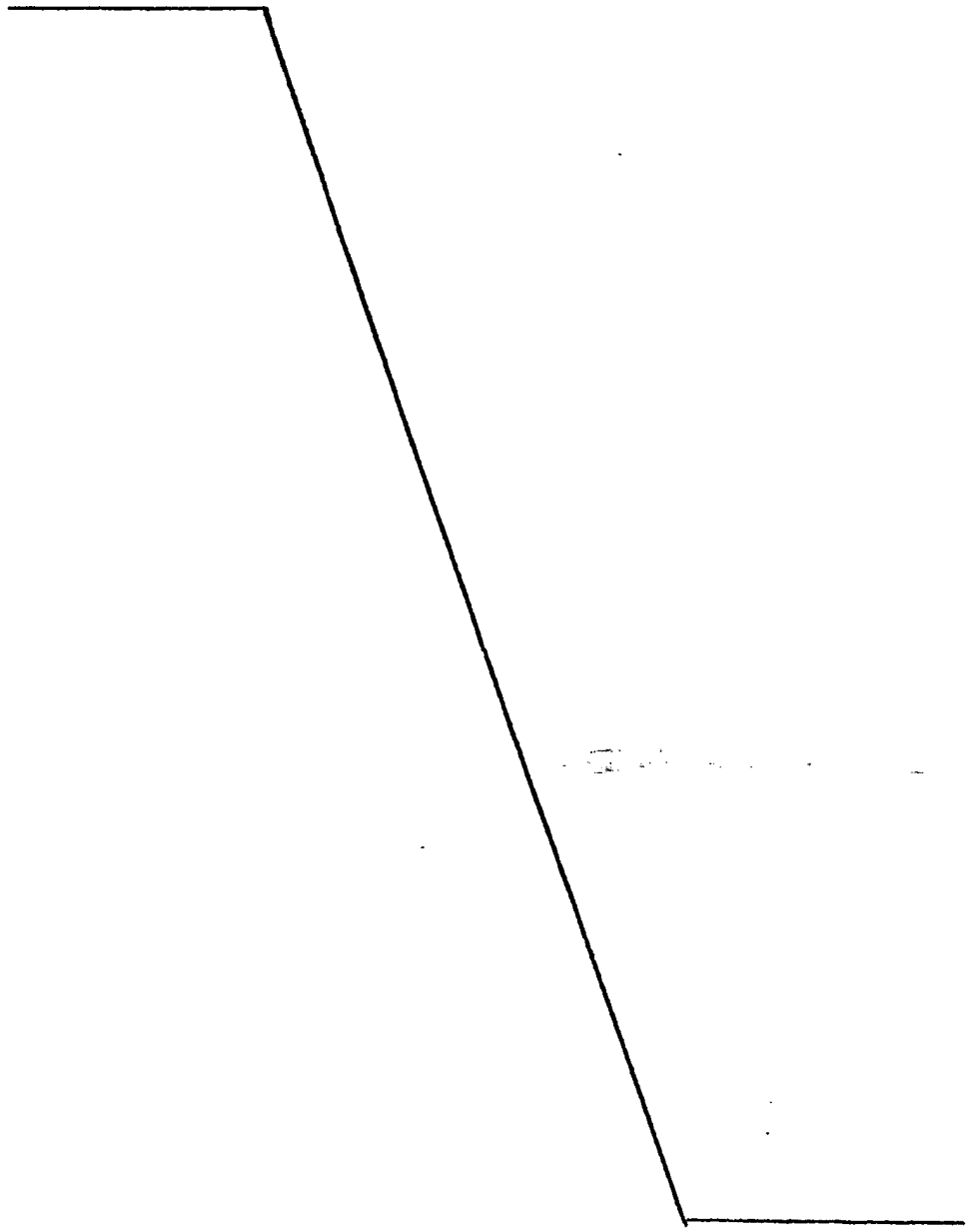
EXAMPLE 21

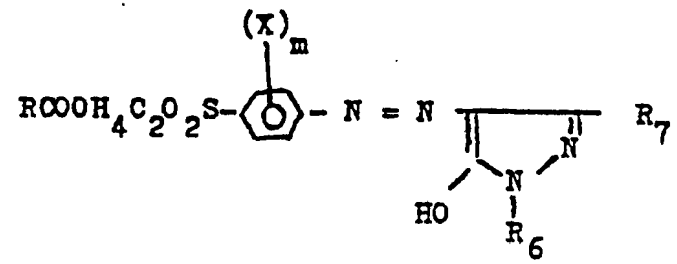
4.52 parts of the anthraquinone intermediate of example 19 were reacted at 80-90°C for 4 hours with 3.0 parts of butyl isocyanate in 20 parts by volume of orthodichloro-benzene.
At the end of the reaction the mass was allowed to cool, then it was filtered and washed with petroleum ether.
After drying, 5.6 parts of the dye :



were obtained which provided a blue shade printing having characteristics similar to the ones of example 19.

Following exactly the modalities described in the preceding examples, the dyes having respectively the following general formulas were obtained :

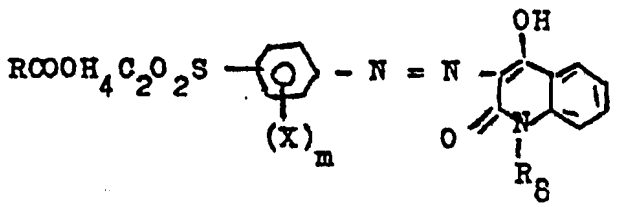




(XI)

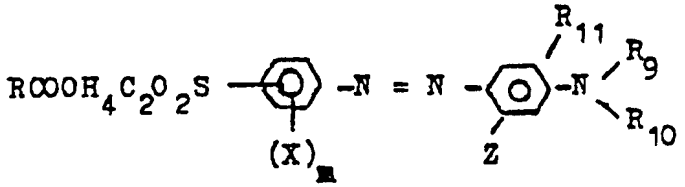
Example No.	R	Chain position	$(X)_m$	R_6	R_7	Shade on blend
22	C_2H_5	meta	2-OCH_3	m-ClC_6H_4	CH_3	yellow
23	CH_3	para	H	2.5-$Cl_2C_6H_3$	CH_3	greenish yellow
24	CH_3O	meta	H	m-$SO_2N(CH_3)_2C_6H_4$	CH_3	yellow
25	CH_3	para	H	C_6H_5	$COOC_2H_5$	yellow
26	C_4H_9NH	para	2-OCH_3; 5-CH_3	C_6H_5	$COOC_2H_5$	golden yellow
27	CH_3	para	2.5-Cl_2	C_3H_7	CH_3	reddish yellow

28	C_3H_7	para	2.6 - Br_2	C_6H_5	CH_3	brownish yellow
29	CH_3	para	H	H	CH_3	yellow
30	CH_3O	meta	2-OCH_3	C_6H_5	$COOC_2H_5$	yellow
31	CH_2=CH-CH_2	para	H	C_6H_5	CH_3	yellow
32	$(CH_3)_3C$	para	H	C_6H_5	CH_3	yellow



(XII)

Example No.	R	Chain position	$(X)_m$	R_8	Shade on blend
33	CH_3	para	H	H	greenish yellow
34	C_2H_5	meta	2-OCH_3	CH_3	yellow
35	C_4H_9O	para	2-OCH_3; 5-CH_3	CH_3	golden yellow
36	C_4H_9	para	2.5-Cl_2	C_2H_5	golden yellow
37	ClC_2H_4NH	meta	H	CH_3	greenish yellow
38	CH_3O	para	H	C_2H_5	greenish yellow
39	CH_3	meta	2-Cl	C_2H_4OH	yellow
40	$(CH_3)_3C$	para	H	CH_3	greenish yellow



(XIII)

Example No.	R	Chain position	$(X)_m$	R_{11}	Z	R_9	R_{10}	Shade on blend
41	C_2H_5	meta	2-OCH_3	H	$NHCOCH_3$	C_2H_5	C_2H_5	orange
42	C_4H_9O	para	H	H	$NHCOC_2H_5$	C_2H_5	C_2H_5	orange
43	CH_3	para	2.5-Cl_2	H	$NHCOC(CH_3)_3$	C_2H_5	C_2H_5	bluish red
44	C_4H_9NH	meta	2-OCH_3	H	CH_3	C_2H_5	C_2H_5	golden yellow
45	CH_3	para	2OCH_3; 5CH_3	H	H	C_2H_4CN	C_2H_4CN	yellow red
46	CH_3O	para	2OCH_3; 5CH_3	H	$NHCOCH_3$	C_2H_4CN	C_2H_5	red
47	CH_3	para	2.6-Br_2	OCH_3	$NHCOCH_3$	CH_3	CH_3	bluish red
48	C_3H_7	para	2.6-Br_2	H	CH_3	C_2H_5	C_2H_5	brownish red

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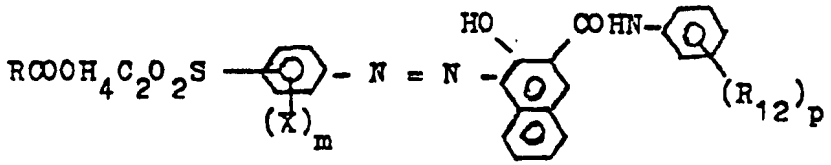
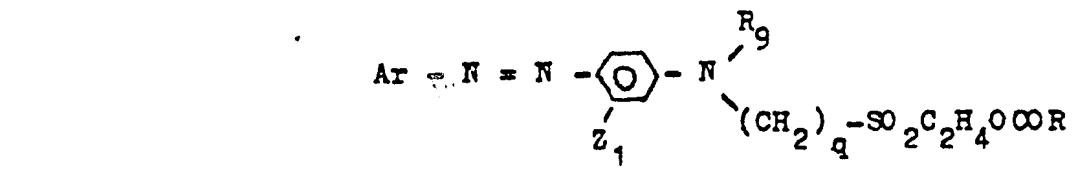
49	ClC_2H_4NH	para	2OCH_3; 5CH_3	H	$NHCOCH_3$	C_2H_4CN	CH_2- 	red-yellow
50	CH_3	meta	H	Cl	CH_3	C_2H_5	C_2H_4OH	red-yellow
51	CH_3	para	H	OCH_3	$NHCOCH_3$	C_2H_5	C_2H_5	red
52	CH_3	para	2-NO_2	H	$NHCOCH_3$	C_2H_4Cl	C_2H_5	bluish red
53	CH_2=CH-CH_2	para	H	H	$NHCOCH_3$	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	reddish yellow
54	CH_3	para	2.6-$(CN)_2$	H	$NHCOCH_3$	C_2H_5	C_2H_5	violet
55	C_2H_5	para	2.6-$(CN)_2$	OCH_3	$NHCOCH_3$	CH_3	CH_3	blue
56	CH_3	para	2OCH_3; 5CH_3	H	$NHCOCH_3$	C_2H_5	C_2H_5	scarlet



(XIV)

Example No.	R	Chain position	$(X)_m$	$(R_{12})_p$	Shade on blend
57	CH_3	para	$2\text{-}OCH_3$; $5\text{-}CH_3$	$2\text{-}OC_2H_5$	red
58	C_3H_7	para	$2\text{-}OCH_3$; $5\text{-}CH_3$	$2\text{-}CH_3$	ruby
59	CH_3O	meta	$2\text{-}OCH_3$	$2\text{-}OCH_3$	scarlet
60	C_4H_9NH	para	H	$2\text{-}CH_3$; $4\text{-}Cl$	scarlet
61	ClC_2H_4NH	para	$2\text{-}OCH_3$; $5\text{-}CH_3$	$3.4\text{-}Cl_2$	bluish red
62	CH_3	para	$2.5\text{-}Cl_2$	$2.4\text{-}(OCH_3)_2$; $5\text{-}Cl$	ruby
63	C_4H_9O	para	$2\text{-}OCH_3$; $5\text{-}CH_3$	$2.5\text{-}(OCH_3)_2$; $4\text{-}Cl$	ruby

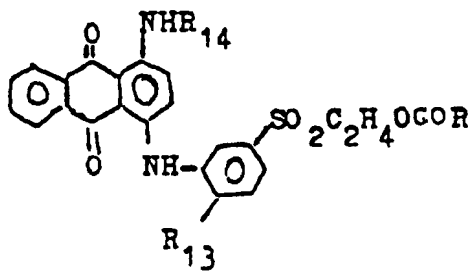
64	$C_4H_9(C_2H_5)CH$	para	H	2.5-$(OCH_3)_2$	scarlet
65	C_4H_9	meta	H	2.5-$(OCH_3)_2$	scarlet
66	C_4H_9NH	para	2-OCH_3; 5-CH_3	H	red
67	$(CH_3)_3C$	meta	2-OCH_3	2.5-$(OCH_3)_2$	scarlet
68	CH_3	meta	2-OCH_3	2-OC_2H_5	reddish orange
69	CH_3	para	2-NO_2	H	violet



(XV)

Example No.	Ar-NH$_2$	R	R_9	q	Z_1	Shade on blend
70	2-cyano-4-nitro-aniline	CH_3	C_2H_5	2	H	ruby
71	2-methylsulphonyl-4-nitro--aniline	C_2H_5	C_2H_5	3	H	violet
72	2-chloro-4-nitro-aniline	C_4H_9NH	C_2H_5	3	CH_3	red
73	2-chloro-4-methylsulphonyl--aniline	CH_3O	C_2H_5	2	CH_3	orange
74	4-nitro-aniline	ClC_2H_4NH	C_2H_4CN	2	Cl	scarlet
75	6-ethoxy-2-amino-benzothiazole	CH_3	C_2H_4OH	2	CH_3	bluish red

76	3-amino-5-nitro-benzoisothiazole	C_4H_9	C_2H_5	3	CH_3	greenish blue
77	2-nitro-4-dimethylaminosulphonyl-aniline	C_4H_9O	C_2H_4CN	2	Cl	reddish brown
78	2.5-dichloro-4-methylsulphonyl-aniline	CH_3	C_2H_5	2	CH_3	brownish red
79	6-methylsulphonyl-2-amino--benzothiazole	C_2H_5	C_2H_5	2	CH_3	ruby
80	2-amino-5-nitro-thiazole	$(CH_3)_3C$	C_2H_5	2	H	blue



(XVI)

Example No.	R	R_{13}	R_{14}	Shade on blend
81	CH_3O	OCH_3	CH_3OOC	reddish blue
82	CH_3	H	H	reddish blue
83	ClC_2H_4NH	OCH_3	ClC_2H_4NHCO	blue
84	CH_3	H	CH_3CO	violet
85	C_4H_9NH	H	C_4H_9NHCO	blue
86	C_4H_9O	H	C_4H_9OOC	reddish blue

87	CH_3	Cl	H	neutral blue
88	C_2H_5	Cl	C_2H_5OO	violet
89	CH_3	CH_3	H	blue
90	C_4H_9NH	CH_3	C_4H_9NHCO	blue
91	C_4H_9O	CH_3	C_4H_9OOC	reddish blue
92	C_2H_5	CH_3	C_2H_5OO	violet

WHAT WE CLAIM IS :

1) Disperse reactive dyes of general formula :

$$D - (SO_2C_2H_4OCOR)_n \qquad (I)$$

wherein :

D is the residue of the molecule of a dye of the azo, anthraquinonic, methinic or quinophthalonic series free from solubilizing groups, such as the sulphonic and the carboxylic groups;

n is a number equal to 1 or 2;

R is an alkyl C_1-C_8, optionally substituted by a halogen or CN; an alkenyl C_2-C_8, optionally substituted by a halogen or CN; an alkoxyl C_1-C_8; a cycloalkoxyl; a HN-alkyl C_1-C_4; a HN-halogen alkyl C_1-C_4; a $N(\text{alkyl } C_1\text{-}C_4)_2$.

2) A process for preparing the dyes of general formula (I), characterized in that an intermediate dye of general formula :

$$D - (SO_2C_2H_4OH)_n \qquad (II)$$

is reacted with a suitable acylating agent such as, for example :

R_1COCl (III) $(R_2)_2NCOCl$ (IV) $(R_3CO)_2O$ (V)

$R_4OOC\text{-}Cl$ (VI) $R_5 - N = C = O$ (VII)

wherein :

D and n have the meanings defined hereinbefore, and :

R_1 is an alkyl C_1-C_8, optionally substituted by a halogen or CN; an alkenyl C_2-C_8, optionally substituted by a halogen or CN;

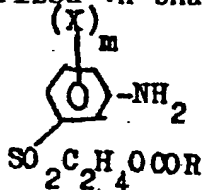
R_2 is an alkyl C_1-C_4;

R_3 is an alkyl C_1-C_8;

R_4 is an alkyl C_1-C_8, optionally substituted by a halogen;

R_5 is an alkyl C_1-C_4; a halogen alkyl C_1-C_4.

3) A process for preparing azoic dyes of general formula (I), characterized in that an amine of general formula :



(VIII)

is diazotized in an aqueous acid medium and the resulting diazo is coupled, always in an aqueous medium, with a suitable coupling intermediate; or an amine of formula :

$$Ar - NH_2 \qquad (IX)$$

is diazotized and its diazonium salt is coupled on a coupling intermediate of formula :

$$Cop - SO_2C_2H_4OCOR \qquad (X)$$

wherein :

R has the meaning defined hereinbefore, and

X is H, a halogen, CN, NO_2, an alkyl C_1-C_4, an alkoxyl C_1-C_4;

m is a number equal to 1 or 2;

Ar is the residue of a diazotizable component of the carbocyclic or heterocyclic series;

Cop is the residue of a coupling component.

4) A process for dyeing and printing, in one step only, polyester-cellulose blended fibres, characterized in that the dyes of general formula (1) are employed.

5) Cellulose materials blended with synthetic materials, in particular polyester-cotton blended fibres, dyed or printed with the dyes according to claim 1.